



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 849 374 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
24.06.1998 Bulletin 1998/26(51) Int. Cl.⁶: C23C 16/40, C23C 16/50,
G02B 1/11

(21) Application number: 97122311.0

(22) Date of filing: 17.12.1997

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE
Designated Extension States:
AL LT LV MK RO SI(30) Priority: 18.12.1996 JP 354141/96
31.10.1997 JP 315992/97(71) Applicant:
DAI NIPPON PRINTING CO., LTD.
Tokyo 162-01 (JP)(72) Inventor:
Ichimura, Koji,
c/o DAI NIPPON PRINTING Co., Ltd.
Tokyo-to (JP)(74) Representative:
Müller-Boré & Partner
Patentanwälte
Grafinger Strasse 2
81671 München (DE)(54) Low refractive Index SiO₂ film and process for producing the same(57) A low refractive index SiO₂ film is provided which uses a starting material for forming an SiO₂ film and has a lower refractive index than the conventional SiO₂ film.

A starting material gas comprising a gas containing a fluorine atom, a gas containing a silicon atom and an alkyl group having 1 to 4 carbon atoms or an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a fluorine atom, and a gas containing an oxygen atom is subjected to plasma CVD in a vacuum chamber 1 to form an SiO₂ film on a web 2 in a plasma zone 5. The SiO₂ film thus formed has, introduced thereto, at least one low refractive index element selected from a fluorine atom, an alkyl group having 1 to 4 carbon atoms, and an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a fluorine atom, and the SiO₂ film with the low refractive index element introduced thereto has a lower refractive index than an SiO₂ film with the low refractive index element not introduced thereto.

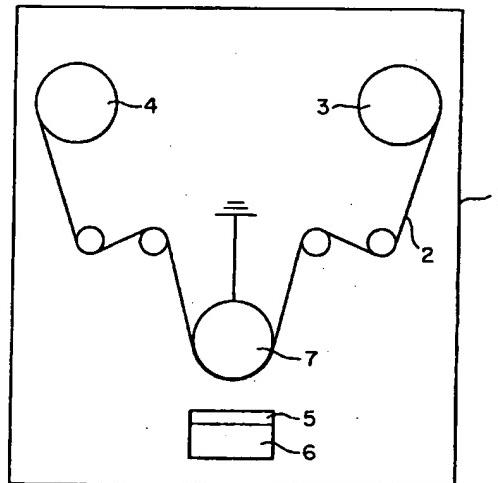


FIG. I

EP 0 849 374 A2

Description

The present invention relates to a low refractive index SiO_2 film which is applicable to a light antireflection film on various surfaces of curve mirrors, back mirrors, goggles, window glasses, displays of personal computers and word processors, and other various commercial displays.

In recent years, antireflection films have been applied to surfaces of various displays of word processors, computers, and televisions, surfaces of various optical lenses and optical articles, and surfaces of window glasses of automobiles and electric railcars to prevent the reflection of light from the above surfaces.

An about 0.1 μm -thick thin film of MgF_2 formed on glass will be described as an example of the antireflection film. It is already known that, when incident light perpendicularly enters a thin film, in order for the antireflection film to prevent the reflection of light by 100% and to pass light by 100% therethrough, relationships represented by the equations (1) and (2) should be met (see "Science Library" Physics = 9 "Optics," pp.70-72, 1980, Science Sha Ltd., Japan).

$$n_0 = \sqrt{n_g} \quad (1)$$

$$n_0 h = \lambda_0 / 4 \quad (2)$$

wherein λ_0 represents a specific wavelength, n_0 represents the refractive index of the antireflection film at this wavelength, h represents the thickness of the antireflection film, and n_g represents the refractive index of the substrate.

It is already known that the refractive index n_g of glass is about 1.5, the refractive index n_0 of MgF_2 film is 1.38, and the wavelength λ_0 of incident light is 5500 Å (reference). When these values are substituted in the equation (2), the results of calculation show that the thickness h of the antireflection film is about 0.1 μm which is the thickness of an optical thin film. For this reason, an optical thin film having such thickness has been used as the antireflection film. Vacuum process, such as vacuum deposition, sputtering, ion plating, and plasma CVD, have been known to be suitable for the formation of such an optical thin film.

From the equation (1), it is apparent that prevention of the reflection of light by 100% can be attained by the selection of such a material that the refractive index of the upper coating is approximately equal to a value of square root of the refractive index of the lower coating. The antireflection of light by utilizing the above principle to make the refractive index of the upper coating lower than the refractive index of the lower coating, that is, by providing a thin film of a high refractive index layer and a thin film of a low refractive index layer in that order on a substrate, has hitherto been performed in the art.

An SiO_2 film is generally known as a low refractive index film and hence has been extensively used as

antireflection films and the like. Antireflection films having various layer constructions, however, have been desired to have lower refractive index.

Accordingly, an object of the present invention is to provide a low refractive index SiO_2 film which uses a starting material for forming an SiO_2 film and has a lower refractive index than the conventional SiO_2 film.

According to one aspect of the present invention, there is provided a low refractive index SiO_2 film comprising an SiO_2 film with a low refractive index element introduced thereto, the low refractive index element being at least one member selected from the group consisting of a fluorine atom, an alkyl group having 1 to 4 carbon atoms, and an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a fluorine atom.

Formation of a film in such a state that at least one low refractive index element selected from the group consisting of a fluorine atom, an alkyl group having 1 to 4 carbon atoms, and an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a fluorine atom is introduced into an SiO_2 -forming material, can provide a film having a lower refractive index than the SiO_2 film *per se*. The SiO_2 film with a low refractive index element introduced thereto according to the present invention has a lower refractive index than the SiO_2 film *per se* and hence is useful as a film as the upper layer in an antireflection film.

An SiO_2 film with a fluorine atom introduced thereto is usually in such a state that a silicon atom is bonded to a fluorine atom. Upon exposure of the SiO_2 film having this bond to an atmosphere having an excessive water vapor content, the bond is likely to be hydrolyzed by moisture in air, causing the low refractive index effect to be lost. Therefore, according to a preferred embodiment of the present invention, an alkyl group with a part or the whole of hydrogen atoms substituted by a fluorine atom is used as the starting material. In this case, the fluorine atom introduced into the SiO_2 film is bonded to the carbon atom, causing no hydrolysis, which permits the low refractive index effect to be maintained for a long period of time.

According to another aspect of the present invention, there is provided a process for producing a low refractive index SiO_2 film, comprising forming a thin film on a substrate by CVD using a starting material gas comprising a gas containing a fluorine atom, a gas containing a silicon atom and an alkyl group having 1 to 4 carbon atoms or an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a fluorine atom, and a gas containing an oxygen atom.

According to a further aspect of the present invention, there is provided a process for producing a low refractive index SiO_2 film, comprising the steps of:

- (1) introducing a mixed gas, comprising a gas containing a fluorine atom, a volatile gas of an organic

compound containing a silicon atom and an alkyl group having 1 to 4 carbon atoms or an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a fluorine atom, and a gas containing an oxygen atom, into a vacuum chamber maintained in a vacuum of 10^{-3} to 1 mmHg (Torr) and bringing the mixed gas to a plasma stream by glow discharge; and

(2) bringing the plasma stream into contact with the surface of a substrate disposed within the vacuum chamber to form a thin film on the substrate.

According to the present invention, since a mixed gas, comprising a gas containing a fluorine atom, a volatile gas of an organic compound containing a silicon atom and an alkyl group having 1 to 4 carbon atoms or an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a fluorine atom, and a gas containing an oxygen atom, is used in the formation of a film by CVD, the resultant CVD film comprises a substantially inorganic SiO₂ film formed by oxidation of Si atom and, introduced into the SiO₂ film, a fluorine atom and/or an alkyl group having 1 to 4 carbon atoms or an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a fluorine atom, that is, a low refractive index element. The SiO₂ film with a low refractive index element introduced thereinto has a lower refractive index than an SiO₂ film not using a gas containing a low refractive index element, that is, an SiO₂ film per se. Further, the low refractive index film has high hardness and bond strength.

Fig. 1 is a schematic diagram showing an embodiment of the construction of a plasma CVD apparatus for producing the low refractive index SiO₂ film according to the present invention.

A schematic diagram showing an embodiment of the construction of a plasma CVD apparatus for producing the low refractive index SiO₂ film according to the present invention is shown in Fig. 1. In Fig. 1, numeral 1 designates a vacuum chamber the interior of which can be regulated to a desired degree of vacuum. A winding/unwinding mechanism containing a pair of rolls 3, 4, which can unwind or rewind a web 2 and function to travel the web 2 in a positive direction or in a reverse direction, is disposed within the vacuum chamber 1. A plasma zone 5 is disposed so as to face the surface of the web 2 travelled between the roll 3 and the roll 4. The plasma zone 5 for plasma CVD treatment comprises a section for projecting a mixed starting material gas, a flat electrode 6, and a film forming drum 7 which can stably travel the web 2 and is grounded. The flat electrode 6 may be a gas projecting electrode which projects an inert gas to create plasma.

A gas containing a fluorine atom, a gas containing a silicon atom and an alkyl group having 1 to 4 carbon atoms or an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a

fluorine atom, and a gas containing an oxygen atom are used as the starting material for forming a low refractive index SiO₂ film by CVD according to the present invention.

The gas containing a fluorine atom is added in order to make the refractive index of the resultant film lower than that of the SiO₂ film per se, and examples thereof include CF₄, C₂F₆, C₃F₆, and SF₆.

The material containing a silicon atom and an alkyl group having 1 to 4 carbon atoms is a main starting material for the low refractive index film. The alkyl group having 1 to 4 carbon atoms, particularly a methyl or ethyl group, is introduced in order to make the refractive index of the resultant film lower than that of the SiO₂ film *per se*. The starting material containing a silicon atom and an alkyl group having 1 to 4 carbon atoms is gasified upon introduction into the vacuum chamber. In the present invention, the reason why the number of carbon atoms of the alkyl group in the material to be gasified is limited to 1 to 4 is that a starting material containing an alkyl group having 5 or more carbon atoms is less likely to be vaporized in CVD, making it difficult to form a low refractive index film.

Gasifiable starting materials containing a silicon atom and an alkyl group having 1 to 4 carbon atoms include silicon-containing organic compounds, such as hexamethyldisiloxane (abbreviation: HMDSO), tetramethylsiloxane (abbreviation: TMDSO), octamethylcyclotetrasiloxane, tetraethoxysilane (abbreviation: TEOS), methyltrimethoxysilane (abbreviation: MTMOS), methylsilane, dimethylsilane, trimethylsilane, diethylsilane, propylsilane, and phenylsilane. Preferred are HMDSO, TMDSO, and TEOS. HMDSO is particularly preferred. For each of these preferred and particularly preferred compounds, the molecule contains an alkyl group having 1 to 4 carbon atoms, such as a methyl or ethyl group, a silicon atom, and an oxygen atom.

According to a further preferred embodiment of the present invention, the material containing a silicon atom and an alkyl group having 1 to 4 carbon atoms as the main starting material is such that a part or the whole of hydrogen atoms in the alkyl group having 1 to 4 carbon atoms has been substituted by a fluorine atom. In this case, the fluorine atom is stably bonded to the carbon atom to offer the effect of stably maintaining the low refractive index effect.

Gasifiable starting materials, containing a silicon atom and an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a fluorine atom, usable herein include HMDSO, TMDSO, octamethylcyclotetrasiloxane, TEOS, MTMOS, methylsilane, dimethylsilane, trimethylsilane, diethylsilane, propylsilane, and phenylsilane, a part or the whole of hydrogen atoms in each of the above compounds being substituted by a fluorine atom.

The gas containing an oxygen atom is used in order to oxidize the Si material to give SiO₂.

Further, other gaseous materials may be added to the mixed gas composed of the above gases from the viewpoint of imparting desired properties.

In the introduction of the mixed gas comprising the Si material gas and the fluorine gas into the vacuum chamber, the flow (SLM) ratio is preferably 1 : 0.1 to 20.

In plasma CVD, the vacuum chamber is preferably kept at a pressure of 10^{-3} to 1 mmHg (Torr).

An antireflection film will be described as a preferred example of products with the low refractive index SiO_2 film, according to the present invention, formed thereon. A polyethylene terephthalate (PET) substrate (a product of Toray Industries, Inc., tradename: Lumirror T-60, thickness: 100 μm) is provided as a substrate. A 125 \AA -thick ITO layer, a 250 \AA -thick SiO_2 layer, a 1000 \AA -thick ITO layer, and a 800 \AA -thick SiO_2 layer are laminated in that order on the PET substrate. The ITO layer may be formed by any means. In general, however, sputtering is applicable. Instead of the ITO layer, a TiO_2 or other layer formed of a high refractive index material may be used. In this case, the higher the degree to which the refractive index of the layer underlying the SiO_2 layer is above the refractive index of the SiO_2 layer, the better the antireflection effect and consequently the better the performance of the antireflection film. Further, when the ITO layer is used, electrical conductivity can be imparted to the film, permitting the film to exhibit an electromagnetic shielding property and an antistatic property. A fluororesin layer having a thickness of not more than 100 \AA may be wet coated thereon from the viewpoint of forming an antismudge coating which functions to enhance the water repellency of the surface, thereby preventing the adhesion of a stain such as a fingerprint.

In the above antireflection film, the ITO layer and the SiO_2 layer, which are first formed on the hard coat layer on the substrate, may be replaced with a wet coat of an organic material. Formation of the ITO layer by sputtering takes a lot of time which is causative of increased production cost. Such a change in film forming means is advantageous from the viewpoint of the cost. The adhesion of the ITO layer formed on the wet coat layer of the organic material is not very good. In this case, a layer having a small thickness (usually not more than 100 \AA) of other material corresponding to an adhesive may be formed between the organic layer and the ITO layer.

If the antireflection property required is not very high (for example, when the formation of a low reflective film is contemplated), an SiO_2 layer alone may be formed on the hard coat. This layer construction is extensively adopted in the antireflection film for LCD from the viewpoint of the cost. In this case, TAC (a product of Fuji Photo Film Co., Ltd., tradename: Fuji Tac, thickness: 100 μm) possessing optical properties, that is, not having birefringence, may be used as the substrate.

The process for producing the low refractive index

SiO_2 film of the present invention by plasma CVD will be described with reference to the following examples.

Example 1

TMDSO, oxygen, and CF_4 were used as starting material gases, and argon was used as a gas for producing plasma. These gases were introduced, as a mixed gas composed of TMDSO (0.1 SLM), oxygen (20 SLM), CF_4 (0.22 SLM), and argon (0.35 SLM), into a vacuum chamber of a plasma CVD apparatus with a pressure regulated to 40 mTorr (4×10^{-2} mmHg), and an electric power of 2.1 kW and 40 kHz was applied between the film forming drum and the gas projecting electrode to produce plasma. On the other hand, a PET film (a product of Toray Industries, Inc., Japan; tradename: Lumirror T-60, thickness: 100 μm) as a substrate was fed into and passed through a plasma producing zone at a feed rate of 1.5 m/min to form an SiO_2 film on the substrate.

The antireflection effect of the SiO_2 film was confirmed as follows. A black vinyl tape was applied to the back surface of the substrate to eliminate the reflection of the back surface. In this state, the reflectance of the front surface in the visible light region was measured at an incident angle of 5°, and the refractive index of the SiO_2 film was evaluated based on the minimum reflectance. As a result, it was found that the minimum reflectance was 1.76% and the refractive index was 1.47.

Comparative Example 1

For comparison, a film of Comparative Example 1 was formed in the same manner as in Example 1, except that CF_4 alone was omitted.

As a result, the SiO_2 film formed without use of CF_4 had a minimum reflectance of 1.95% and a refractive index of 1.483. Thus, the SiO_2 film formed using CF_4 in Example 1 had lower reflectance and lower refractive index.

Example 2

Oxygen was used as a part of the starting material, and argon was used as a carrier gas for producing plasma. These gases were introduced, as a mixed gas composed of oxygen (30 sccm) and argon (30 sccm), into a vacuum chamber of a plasma CVD apparatus with a pressure regulated to 40 mTorr. HMDSO (hexamethyldisiloxane) as a monomer material was bubbled by this carrier gas to feed the monomer material into the vacuum chamber of the CVD apparatus with a pressure regulated to 40 mTorr. The bubbling temperature was room temperature. Plasma was produced by applying an electric power of 100 W and 13.56 MHz across the upper electrode and the earth electrode.

A PET film [a product of Toray Industries, Inc., tradename: Lumirror T-60, thickness: 100 μm] was used

as a substrate, and the film formation time was 10 min. The refractive index of the film thus formed was measured by ellipsometry and found to be 1.42. The film was analyzed by IR spectrometry for the presence of a CH₃ group. As a result, a peak derived from stretching of an Si-CH₃ bond appeared around 1277 cm⁻¹, indicating the presence of the CH₃ group.

Comparative Example 2

For comparison, the procedure of Example 2 was repeated, except that the flow rate of oxygen was 100 sccm. Thus, an SiO₂ film of Comparative Example 2 was formed. The SiO₂ film was analyzed by IR spectroscopy. As a result, the presence of a CH₃ group was hardly observed. The refractive index of the SiO₂ film formed in Comparative Example 2 was measured by ellipsometry and found to be 1.44, which was higher than the refractive index of the SiO₂ film, with the CH₃ group introduced thereto, prepared in Example 2.

Example 3

A PET film (a product of Toray Industries, Inc., tradename: Lumirror T-60, thickness: 100 µm) was provided as a substrate. Oxygen, argon, and CF₄ were used as the starting material gases. Further, HMDSO (hexamethyldisiloxane) was used as the monomer material. The gas flow rate was 30 sccm for oxygen, 30 sccm for argon, and 30 sccm for CF₄. The monomer material was bubbled using the argon gas as a carrier gas and fed into a vacuum chamber of a plasma CVD apparatus with the pressure being regulated to 40 mTorr. The bubbling temperature was room temperature.

An electric power of 100 W and 13.56 MHz was applied across the upper electrode and the earth electrode to produce plasma. The film formation time was 10 min. The refractive index of the SiO₂ film with fluorine atom introduced thereto was measured by ellipsometry and found to be 1.40.

Comparative Example 3

For comparison, in the formation of an SiO₂ film, CF₄ was not used to form an SiO₂ film with a fluorine atom not introduced thereto, and the refractive index of the SiO₂ film with no fluorine atom introduced thereto was measured by ellipsometry and found to be 1.42, which was higher than the refractive index (1.40) of the SiO₂ film, with the fluorine atom introduced thereto, prepared in Example 3.

Example 4

A PET film (a product of Toray Industries, Inc., tradename: Lumirror T-60, thickness: 100 µm) was provided as a substrate. Oxygen and argon were used as

the starting material gases. Further, HMDSO (hexamethyldisiloxane) with H in the CH₃ thereof being substituted by F was used as the monomer material. The gas flow rate was 30 sccm for oxygen and 30 sccm for argon. The monomer material was bubbled using the argon gas as a carrier gas and fed into a vacuum chamber of a plasma CVD apparatus with the pressure being regulated to 40 mTorr. The bubbling temperature was room temperature.

10 An electric power of 100 W and 13.56 MHz was applied across the upper electrode and the earth electrode to produce plasma. The film formation time was 10 min. The refractive index of the SiO₂ film was measured by ellipsometry and found to be 1.40.

15 For both the SiO₂ film formed in this example (Example 4) and the SiO₂ film formed in Example 3, the initial refractive index was 1.40. These SiO₂ films were allowed to stand for three days under high temperature and high humidity conditions (80°C, 95% RH). As a result, the SiO₂ film formed in Example 4 underwent no change in refractive index, whereas the refractive index of the SiO₂ film prepared in Example 3 was increased to 1.45. This demonstrates that, in the SiO₂ film with a fluorine atom introduced thereto, use of HMDSO, with H in the CH₃ group substituted by F, rather than use of CF₄ resulted in better high temperature and high moisture resistance.

20 The refractive index SiO₂ film with at least one low refractive index element selected from a fluorine atom, an alkyl group having 1 to 4 carbon atoms, and an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms thereof being substituted by a fluorine atom has lower refractive index than the SiO₂ film with no low refractive index element introduced thereto.

Claims

1. A low refractive index SiO₂ film comprising an SiO₂ film with a low refractive index element introduced thereto, the low refractive index element being at least one member selected from the group consisting of a fluorine atom, an alkyl group having 1 to 4 carbon atoms, and an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a fluorine atom.
2. The low refractive index SiO₂ film according to claim 1, which is adapted for use as an antireflection film.
3. The low refractive index SiO₂ film according to claim 1 or 2, which has been prepared by CVD using at least one starting material selected from the group consisting of a gas containing a fluorine atom, a starting material containing a silicon atom and an alkyl group having 1 to 4 carbon atoms, and a starting material containing a silicon atom and an

alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a fluorine atom.

4. The low refractive index SiO₂ film according to one or more of claims 1 to 3, wherein the gas containing fluorine atoms is selected from the group consisting of CF₄, C₂F₆, C₃F₆, and SF₆. 5
5. The low refractive index SiO₂ film according to one or more of claims 1 to 4, wherein the starting material containing a silicon atom and an alkyl group having 1 to 4 carbon atoms comprises at least one compound selected from the group consisting of HMDSO, TMDSO, octamethylcyclotetrasiloxane, TEOS, MTMOS, methylsilane, dimethylsilane, trimethylsilane, diethylsilane, propylsilane, and phenylsilane. 10
6. The low refractive index SiO₂ film according to one or more of claims 1 to 5, wherein the starting material containing a silicon atom and an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a fluorine atom comprises at least one compound selected from the group consisting of HMDSO, TMDSO, octamethylcyclotetrasiloxane, TEOS, MTMOS, methylsilane, dimethylsilane, trimethylsilane, diethylsilane, propylsilane, and phenylsilane, a part or the whole of hydrogen atoms in each of said compounds being substituted by a fluorine atom. 15
7. A process for producing a low refractive index SiO₂ film, comprising forming a thin film on a substrate by CVD using a starting material gas comprising a gas containing a fluorine atom, a gas containing a silicon atom and an alkyl group having 1 to 4 carbon atoms or an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a fluorine atom, and a gas containing an oxygen atom. 20
8. A process for producing a low refractive index SiO₂ film, comprising the steps of: 25
- (1) introducing a mixed gas, comprising a gas containing a fluorine atom, a volatile gas of an organic compound containing a silicon atom and an alkyl group having 1 to 4 carbon atoms or an alkyl group having 1 to 4 carbon atoms with a part or the whole of hydrogen atoms substituted by a fluorine atom, and a gas containing an oxygen atom, into a vacuum chamber maintained in a vacuum of 10⁻³ to 1 mmHg (Torr) and bringing the mixed gas to a plasma stream by glow discharge; and 30
- (2) bringing the plasma stream into contact with the surface of a substrate disposed within

the vacuum chamber to form a thin film on the substrate.

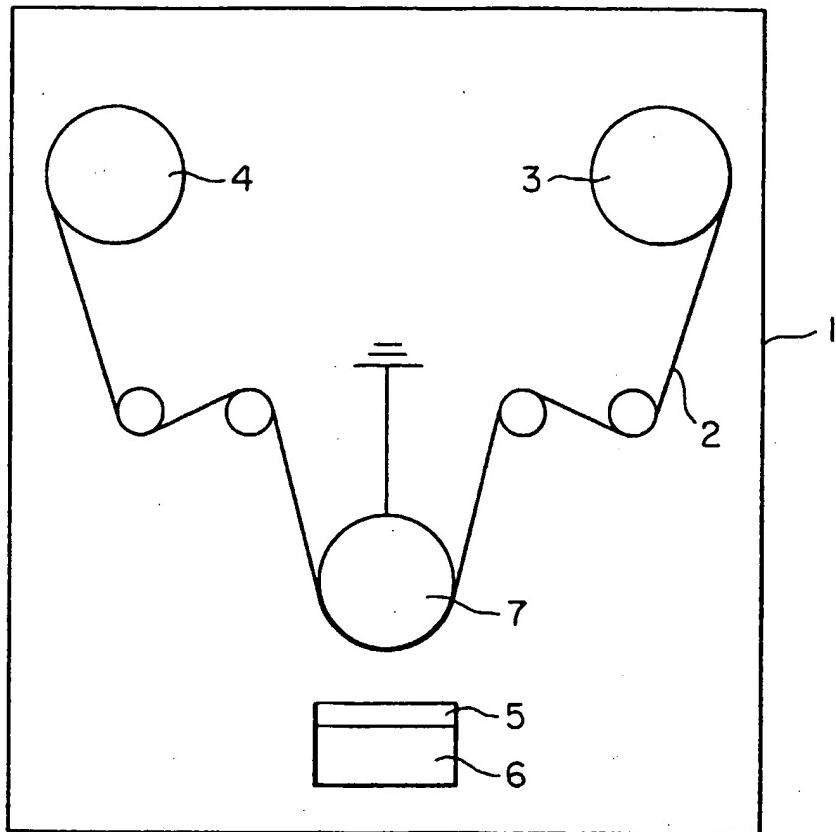


FIG. I

THIS PAGE BLANK (USPTO)